Acid-Catalyzed Olefin–Alcohol Interconversion in the 1-Methylcyclooctyl System. Strain-Relief Acceleration of the Hydration of 1-Methyl-*trans*-cyclooctene[1]

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Rates of reaction with aqueous perchloric acid at 25 °C have been measured for 1-methyl-*cis*-cyclooctene, 1-methyl-*trans*-cyclooctene, and their exo isomer, methylenecyclooctane. The only products formed to any significant extent in each of these reactions are 1-methylcyclooctanol and the *cis*-cycloalkene, but both the *trans*- and *exo*-olefins give these products in initially nonequilibrium proportions: [ROH]/[CIS] = 1.27 ± 0.05 at equilibrium, 15.1 ± 0.9 from the *trans*-olefin and 0.44 ± 0.05 from the *exo*-olefin. This is taken as evidence for the existence of two conformationally different 1-methylcyclooctyl carbocationic intermediates in these reactions, an unstable crown (or twist) cation formed by protonation of the *trans*-olefin and a (conformationally) stable boat–chair cation formed from the other two olefins and the alcohol. The barrier for interconversion of these two cations is estimated at $\Delta G^{\ast} = 5.3 \pm 0.6$ kcal mol^{-1}. The barrier for hydration of either cation to the alcohol is also estimated, by two different methods, at $\Delta G^{\ast} = 3.6 \pm 0.6$ kcal mol^{-1} or 4.3 ± 0.3 kcal mol^{-1}. The smallness of these barriers suggests that the reaction of tertiary aliphatic carbocations with water in aqueous solution is an essentially unactivated process. These estimates plus the rate and equilibrium constants measured here allow a nearly complete free energy characterization of the 1-methylcyclooctyl system. The rates of reaction of the *cis*- and *exo*-olefin with the hydronium ion are normal, but strain relief accelerates the rate of the *trans*-cycloalkene by a factor of 18 500.

The acid-catalyzed hydration of carbon–carbon double bonds is an elementary chemical transformation of considerable importance whose mechanism has excited the interest of various investigators over the past century.[2] Simple unstrained olefins are only moderately reactive in this process and undergo hydration at conveniently measured rates only in concentrated aqueous acids, where interpretation of experimental results is less straightforward than in dilute solution. We have therefore sought out and examined examples of this process in which reaction is accelerated by various means. In this paper we report the results of our study of 1-methyl-*trans*-cyclooctene, 1.
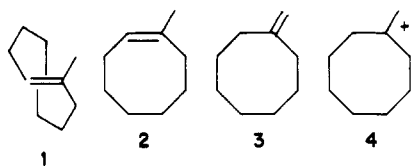
The trans double bond of this olefin is twisted significantly,[3] and the strain thus produced is relieved in the course of its hydration. Similar distortion of the double bond in the parent substance, *trans*-cyclooctene itself, which is the smallest isolable *trans*-cycloalkene,[4] developes strain which can be estimated at about 10 kcal mol^{-1}.[5]

In the course of carrying out this investigation of 1-methyl-*trans*-cyclooctene, we found it instructive to examine the acid-catalyzed hydration of its cis and exo isomers as well, 1-methyl-*cis*-cyclooctene, 2, and methylenecyclooctane, 3. The result is an almost complete characterization in terms of rate and equilibrium constants for interconversion of all of the olefin and alcohol species directly related to the 1-methylcyclooctyl carbocation, 4.

Experimental Section

Materials. 1-Methyl-*trans*-cyclooctene was made by the olefin inversion method of Bridges and Whitham[6] by using hydroxyphosphine oxide precursor kindly supplied by Dr. Whitham. 1-Methylcyclooctanol was prepared by treating cyclooctanone with methylmagnesium iodide, and 1-methyl-*cis*-cyclooctene was obtained by dehydrating this alcohol.[7] Methylenecyclooctane was synthesized by a Wittig reaction between cyclooctanone and methyltriphenylphosphonium chloride. All of these substances had physical properties consistent with literature values and gave NMR spectra appropriate for their structures; samples used for quantitative measurements were purified by gas chromatography. All other materials were best available commercial grades.

Solutions were prepared by using deionized water purified further by distillation from alkaline permanganate.

Extinction Coefficients. Extinction coefficients of the UV absorption bands of the olefins were measured with a Cary Model 118C spectrometer with cell compartment thermostatted at 25.0 ± 0.02 °C. A stock solution of olefin of known concentration (ca. 0.02 M) in ethanol was prepared accurately by weight, and 1.00-μL aliquots of this solution were added sequentially to a known weight of water (ca. 3.5 g) contained in a spectrometer cuvette; these additions were performed with a Hamilton CR-700-20 constant rate syringe with spring-loaded drive. The calibration of this syringe was checked by weighing delivered amounts of water; it was found to be accurate to 1%, as claimed by the manufacturer. After each addition, absorbances of the solutions were measured at 2-nm intervals in the region λ 196–210 nm. Ten such dilutions followed by absorption measurements were generally made for a given substrate, and Beer's law plots of absorbance vs. olefin concentration were constructed from the data so obtained. These were found to be accurately linear, and extinction coefficients were evaluated as their slopes by least-squares analysis.

Product Compositions. The compositions of the product mixtures found in the hydration of 1-methyl-*trans*-cyclooctene and 1-methyl-*cis*-cyclooctene and the dehydration of 1-methylcyclooctanol were determined spectrophotometrically. Since the cis isomer is the only one of the three olefins of the 1-methylcyclooctyl system (cis, trans, and exo) which is present in significant amount in an equilibrated *cis*-olefin/alcohol mixture or as the product of *trans*-olefin hydration (see below), and since the alcohol does not absorb light at the wavelengths used (196–210

(1) Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, IL, Sept, 1977, Abstracts, ORGN 047.

(2) For a recent review see: Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* 1977, *10*, 252–258.

(3) Traetteberg, M.; Bakken, P. *J. Mol. Struct.* 1981, *74*, 321–330.

(4) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 112.

(5) Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* 1957, *79*, 4133–4136.

(6) Bridges, A. J.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* 1974, 142–143.

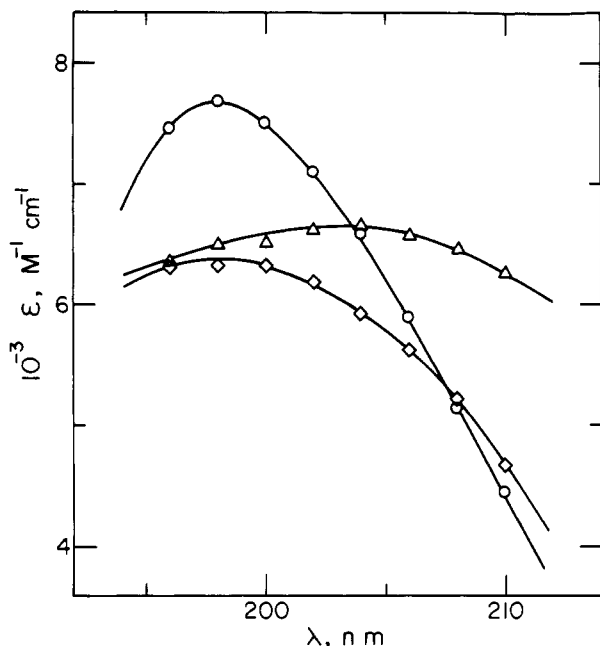(7) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* 1952, *74*, 1894–1902.

Figure 1. Extinction coefficients for the olefins of the 1-methylcyclooctyl system in aqueous solution at 25 °C: (O) 1-methyl-*cis*-cyclooctene; (Δ) 1-methyl-*trans*-cyclooctene; (◊) methylenecyclooctane.

Table I. Product Compositions Determined for Acid-Catalyzed Reactions of the 1-Methylcyclooctyl System in Aqueous Solution at 25 °C

starting substrate	catalyst (HClO$_4$) concn, M	[ROH]/[CIS]
1-methyl-*cis*-cyclooctene	0.5–2.7	1.27 ± 0.05[a]
1-methyl-*cis*-cyclooctene	2.4	1.36 ± 0.02[b,c]
1-methylcyclooctanol	0.4–2.0	1.17 ± 0.07[a]
1-methyl-*trans*-cyclooctene	0.02	15.1 ± 0.9[b,d]
1-methyl-*trans*-cyclooctene	1.2	1.26 ± 0.02[b,c]
1-methyl-*trans*-cyclooctene	2.4	1.20 ± 0.02[b,c]

[a] Determined at λ 200 nm with A_∞ values from kinetic runs. [b] Determined at eight wavelengths in the range λ 196–210 nm. [c] Determined on equilibrated solutions. [d] Determined after all *trans*-olefin had been consumed but before true equilibration had begun.

nm), *cis*-olefin concentrations could be calculated from final absorbance readings by using the extinction coefficients for 1-methyl-*cis*-cyclooctene determined here; alcohol concentrations were then obtained by difference from known initial substrate concentrations. These determinations were made either on solutions employed for kinetic runs using "infinite time" absorbance readings, A_∞, made at a single wavelength, or on solutions allowed to stand for at least ten reaction half-lives; in the latter case, absorbances were measured at 2-nm intervals in the range λ 196–210 nm, as for the extinction coefficient determinations.

Kinetics. Rate constants were measured spectrophotometrically by monitoring the appearance or disappearance of olefin absorption, either at λ 200 or 205 nm for 1-methyl-*trans*-cyclooctene, λ 200 nm for 1-methyl-*cis*-cyclooctene, or λ 207 nm for the exo isomer, methylenecyclooctane. A Cary Model 118C spectrometer was used for the slower reactions and a Durrum-Gibson stopped-flow spectrometer for the faster runs. Both machines were operated with cell compartments at 25.0 ± 0.05 °C. For the experiments using the Cary spectrometer, a known weight of acid catalyst solution (ca. 3.5 g) contained in a 1-cm spectrometer cuvette was first allowed to come to temperature equilibrium with the cell compartment. An aliquot, usually 10 μL, of ethanol solution of substrate of known concentration was then injected into the acid solution with a calibrated Hamilton CR-700-20 constant rate syringe, the resulting mixture was shaken to effect solution, and absorbance measurements, A, were begun. These measurements were continued for at least three half-lives and "infinite time" readings, A_∞, were made after at least ten half-lives.

In the runs with the Durrum-Gibson stopped-flow spectrometer, equal volumes of aqueous substrate and acid solutions were mixed and an oscilloscope was used to record absorbance as a function of time. The oscilloscope trace was then photographed and data points were subsequently read off this photograph.

The data for hydration of the *cis*- and *trans*-olefins, as well as those for dehydration of the alcohol 1-methylcyclooctanol, obeyed the first-order rate law well. In these cases first-order rate constants were evaluated as slopes of plots of ln $(A - A_\infty)$ vs. time. The data for hydration of the *exo*-olefin, methylenecyclooctane, on the other hand, showed biphasic behavior; this case was treated as described below.

Results

Extinction Coefficients. Extinction coefficient determinations were made for each of the three isomeric

olefins in the 1-methylcyclooctyl system, cis, trans, and exo, at eight wavelengths spaced at 2-nm intervals over the region λ 196–210 nm. The data are summarized in Table S1[8] and are illustrated in Figure 1. They give the following aqueous solution absorption maxima: 1-methyl-*cis*-cyclooctene, λ_{max} 198 nm, ϵ_{max} 7.7 × 10^3 M^{-1} cm^{-1}; 1-methyl-*trans*-cyclooctene, λ_{max} 204 nm, ϵ_{max} 6.6 × 10^3 M^{-1} cm^{-1}; methylenecyclooctane, λ_{max} 198 nm, ϵ_{max} 6.4 × 10^3 M^{-1} cm^{-1}. The cis and exo isomers have equal extinctions, ϵ 5.5 × 10^3 M^{-1} cm^{-1}, at λ 207 nm.

Product Composition. It is well-known that the exocyclic double bonds in methylenecycloalkanes are less stable than those in their endocyclic 1-methylcycloalkene isomers, and direct measurement has shown that the exo:endo ratio for the cyclooctyl system in acetic acid solution at 25 °C is 1:600.[9] The proportion of *exo*-olefin at equilibrium in aqueous solution at 25 °C must be at least as small as this, for using gas chromatographic detection, we were unable to find any methylene cyclooctane in a mixture of 1-methyl-*cis*-cyclooctene and 1-methylcyclooctanol which had been allowed to equilibrate in aqueous acid at this temperature. 1-Methyl-*trans*-cyclooctene was also absent from this mixture, in keeping with its instability. The only 1-methylcyclooctyl species present to any significant extent at equilibrium in aqueous solution at 25 °C are thus the *cis*-olefin and the alcohol.

We determined the equilibrium amounts of alcohol to *cis*-olefin in this medium by approaching equilibrium from the olefin and also from the alcohol side and by making absorption measurements at multiple wavelengths on spent reaction mixtures as well as by using single wavelength "infinite time" absorbance readings from kinetic runs. The data, summarized in the first three entries of Table I, show good consistency and no discernable trend with acid concentration up to 2.7 M HClO$_4$; they give [ROH]/[CIS] = 1.27 ± 0.05 as the best value of the equilibrium constant relating 1-methylcyclooctanol and 1-methyl-*cis*-cyclooctene in dilute to moderately concentrated aqueous acid at 25 °C.

Because 1-methyl-*trans*-cyclooctene is strained, it reacts with aqueous acid much faster than does the cis isomer, and its conversion to alcohol and *cis*-olefin is complete before equilibration of these two products has begun. It is therefore possible, by working in sufficiently dilute acid, to measure the ratio of alcohol to *cis*-olefin products formed directly from the *trans*-olefin. The value so obtained, [ROH]/[CIS] = 15.1 ± 0.9, is decidely different

(8) Supplementary material. See paragraph at end of paper regarding this material.
(9) Cope, A. C.; Ambros, D.; Ciganek, E.; Howell, C. F.; Jacura, Z. *J. Am. Chem. Soc.* **1959**, *81*, 3153–3154; *J. Am. Chem. Soc.* **1960**, *82*, 1750–1753.
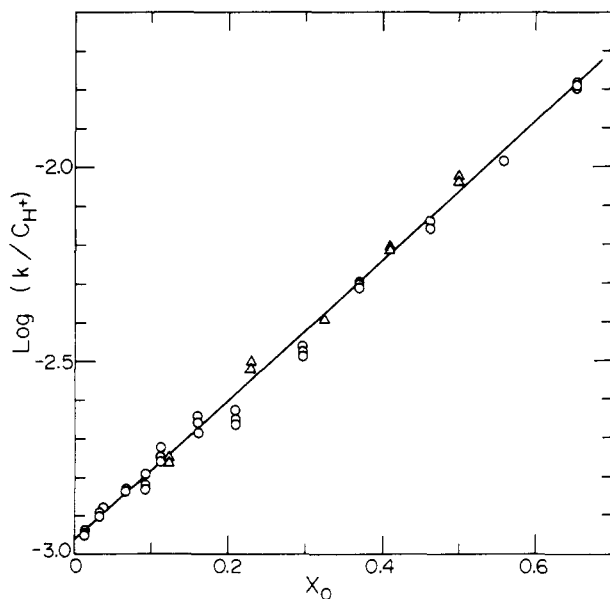
Figure 2. Rates of approach to equilibrium in the 1-methyl-*cis*-cyclooctene–1-methylchclooctanol system: (O) starting substrate = 1-methyl-*cis*-cyclooctene; (Δ) starting substrate = 1-methylcyclooctanol.

Figure 3. Relationship between acid concentration and observed first-order rate constants for the first, fast phase of the reaction of 1-methyl-*trans*-cyclooctene with aqueous perchloric acid.

from the equilibrium ratio of 1.27 ± 0.05. In moderately concentrated acids, on the other hand, reaction of the first-formed products is more rapid, and, as the last two entries of Table I show, the final values of [ROH]/[CIS] obtained here correspond to true equilibrium.

Kinetics. 1-Methyl-*cis*-cyclooctene. Rates of approach to equilibrium in the 1-methyl-*cis*-cyclooctene/1-methylcyclooctanol system were measured by using both the alcohol and the olefin as the starting material. In each case, the absorbance of the reaction solution changed smoothly and followed a single exponential rate law. The reactions were acid catalyzed and measurements were made in the range $[HClO_4]$ = 0.05–2.7 M for runs with the olefin as starting substrate and $[HClO_4]$ = 0.4–2.0 M for those beginning with the alcohol. These data are summarized in Table S2.[8]

As is usually the case for reactions of this kind in moderately concentrated acid solution, first-order rate constants increased with acidity considerably more strongly than in direct proportionality to the first power of acid concentration, and an acidity function had to be used to correlate the data. The X_0 function,[10] which appears to be the best currently available measure of the acidity of concentrated aqueous perchloric acid solutions,[11] was used for this purpose. This function gave good linear relations: $\log (k/C_{H^+})$ = -3.014 ± 0.007 + (1.76 ± 0.02)X_0 for runs with the olefin as starting substrate and $\log (k/C_{H^+})$ = -2.998 ± 0.033 + (1.85 ± 0.09)X_0 for those beginning with the alcohol. The parameters of these two relationships are the same within experimental error, as expected for true approach to equilibrium, and the two sets of data were therefore combined into a single correlation. This, $\log (k/C_{H^+})$ = -3.016 ± 0.008 + (1.80 ± 0.02)X_0, is shown in Figure 2; it gives k_{H^+} = (9.63 ± 0.17) × 10^{-4} M^{-1} s^{-1} as the extrapolated value of the specific rate of approach to equilibrium catalyzed by the hydronium ion in dilute solution.

This rate constant is, of course, the sum of specific rates for the forward and reverse reactions in this equilibrating
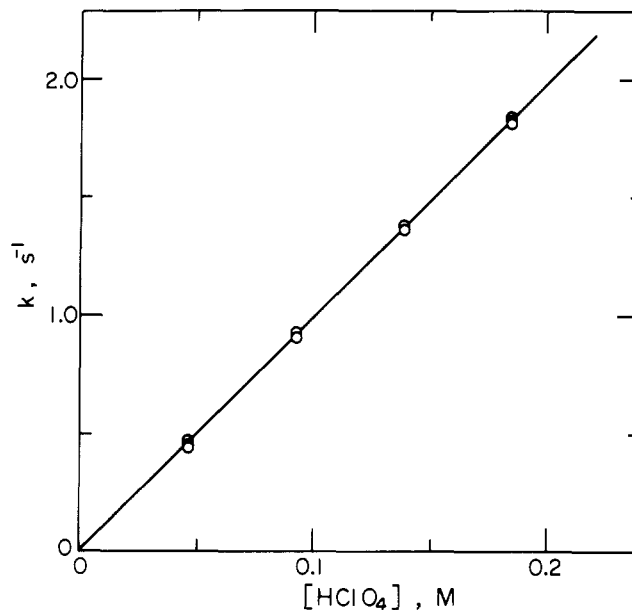
system. It can be separated into its constituents, $k^f_{H^+}$ and $k^r_{H^+}$ by using the equilibrium constant determined above, K = 1.27 ± 0.05 = $k^f_{H^+}/k^r_{H^+}$. This gives $k^f_{H^+}$ = (5.38 ± 0.14) × 10^{-4} M^{-1} s^{-1} as the hydronium ion catalytic coefficient for conversion of 1-methyl-*cis*-cyclooctene to 1-methylcyclooctanol and $k^r_{H^+}$ = (4.25 ± 0.13) × 10^{-4} M^{-1} s^{-1} as that for conversion of 1-methylcyclooctanol to 1-methyl-*cis*-cyclooctene.

1-Methyl-*trans*-cyclooctene. The reaction of this substrate with aqueous acid consisted of two phases: an inital fast conversion of the *trans*-olefin to a nonequilibrium mixture of 1-methyl-*cis*-cyclooctene plus 1-methylcyclooctanol, followed by a slower adjustment of the concentrations of these products to equilibrium proportions. The time constants of these two phases were so different (10 000:1) that the data could easily be fitted to separate exponential functions by conventional first-order kinetic means.

The first phase was fast enough to require use of stopped-flow apparatus. The process was acid catalyzed, and measurements were made in the range $[HClO_4]$ = 0.05–0.2 M. The data fit the first-order rate law well and gave ratio constants, summarized in Table S3,[8] which are directly proportional to acid concentration (Figure 3). Least-squares analysis produced the hydronium ion catalytic coefficient k_{H^+} = 9.93 ± 0.04 M^{-1} s^{-1}.

In the second phase of this reaction, the absorbance (at λ 200 nm) increased, rather than decreased as it did during the first phase, and reached a final value consistent with the equilibrium *cis*-olefin:alcohol ratio, determined as described above. The rate of approach to this final absorbance value was also in good agreement with the independently determined rate of equilibration of *cis*-olefin and alcohol. The data, summarized in Table S4,[8] were again correlated with the X_0 function. The result, $\log (k/C_{H^+})$ = -2.996 ± 0.026 + (1.89 ± 0.07)X_0, gives k_{H^+} = (10.0 ± 0.6) × 10^{-4} M^{-1} s^{-1} as the extrapolated value of the hydronium ion catalytic coefficient in dilute solution; this is in good agreement with k_{H^+} = (9.63 ± 0.17) × 10^{-4} M^{-1} s^{-1} obtained from the *cis*-olefin/alcohol equilibration experiments.
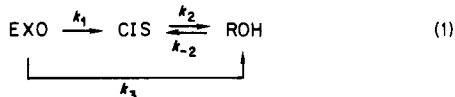
Methylenecyclooctane. The reaction of this olefin with aqueous perchloric acid was also biphasic: the ab-

(10) Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116–2124.
(11) Kresge, A. J.; Chen, H. J.; Capen, G. L.; Powell, M. F. *Can. J. Chem.* **1983**, *61*, 249–256.

sorbance of a reaction mixture first dropped by about 40% and then continued to decrease another 15% at a distinctly slower rate. The final absorbance value was characteristic of the position of equilibrium between 1-methyl-*cis*-cyclooctene and 1-methylcyclooctanol. The time constants of the two reaction phases in this case were not strongly different, and the data could not be fitted successfully to two simple first-order functions. The system was therefore analyzed in a different way on the basis of the following reaction model.

The simplest scheme consistent with this observed biphasic behavior is reaction of the exocyclic olefin (EXO) to give the cis isomer (CIS) and alcohol (ROH) in nonequilibrium proportions, followed by equilibration of these two products at a slower rate. This is shown in eq 1. At

$$\text{EXO} \xrightarrow{k_1} \text{CIS} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{ROH} \qquad (1)$$

$$\underbrace{\phantom{\text{EXO} \xrightarrow{k_1} \text{CIS} \rightleftharpoons \text{ROH}}}_{k_3}$$

a given acid concentration, EXO will disappear by the two parallel first-order reactions whose rate constants are k_1 and k_3; its concentration will consequently follow the simple exponential rate law given as eq 2. Equation 3

$$[\text{EXO}] = [\text{EXO}]_0 e^{-(k_1+k_3)t} \qquad (2)$$

$$\frac{d[\text{CIS}]}{dt} = k_1[\text{EXO}] - k_2[\text{CIS}] + k_{-2}[\text{ROH}] \qquad (3)$$

describes the behavior of CIS. Combination of this with the equilibrium relationship of eq 4 and the mass balance expression of eq 5 ($[\text{EXO}]_e = 0$) then leads to eq 6, which can be integrated. The result is the double exponential

$$[\text{ROH}]_e/[\text{CIS}]_e = k_2/k_{-2} \qquad (4)$$

$$[\text{EXO}] + [\text{CIS}] + [\text{ROH}] = [\text{CIS}]_e + [\text{ROH}]_e \qquad (5)$$

$$\frac{d[\text{CIS}]}{dt} = (k_1 - k_{-2})[\text{EXO}]_0 e^{-(k_1+k_3)t} - (k_2 + k_{-2})([\text{CIS}] - [\text{CIS}]_e) \qquad (6)$$

$$[\text{CIS}] - [\text{CIS}]_e = \frac{(k_{-2} - k_1)[\text{EXO}]_e}{k_1 - k_2 - k_{-2} + k_3} e^{-(k_1+k_3)t} - \left\{ \frac{(k_{-2} - k_1)[\text{EXO}]_0}{k_1 - k_2 - k_{-2} + k_3} + [\text{CIS}]_e \right\} e^{-(k_2+k_{-2})t} \qquad (7)$$

rate law of eq 7. When this is added to eq 2, the result is an expression, eq 8, for the difference between the total olefin concentration at any time, $[\text{EXO}] + [\text{CIS}]$, and its equilibrium value, $[\text{CIS}]_e$. This is the quantity which was mentioned in these experiments.

$$[\text{EXO}] + [\text{CIS}] - [\text{CIS}]_e = \frac{(k_3 - k_2)[\text{EXO}]_0}{k_1 - k_2 - k_{-2} + k_3} e^{-(k_1+k_3)t} + \left\{ \frac{(k_1 - k_{-2})[\text{EXO}]_0}{k_1 - k_2 - k_{-2} + k_3} + [\text{CIS}]_e \right\} e^{-(k_2+k_{-2})t} \qquad (8)$$

This was accomplished by making measurements at a wavelength, λ 207 nm, where the extinction coefficients of EXO and CIS have the same value, ϵ. Under this condition, $([\text{EXO}] + [\text{CIS}]) = A/\epsilon$, $[\text{CIS}]_e = A_\infty/\epsilon$, and $[\text{EXO}]_0 = A_0/\epsilon$, and eq 8 reduces to eq 9.

$$A - A_\infty = \frac{(k_3 - k_2)A_0}{k_1 - k_2 - k_{-2} + k_3} e^{-(k_1+k_3)t} + \left\{ \frac{(k_1 - k_{-2})A_0}{k_1 - k_2 - k_{-2} + k_3} - A_\infty \right\} e^{-(k_2+k_{-2})t} \qquad (9)$$
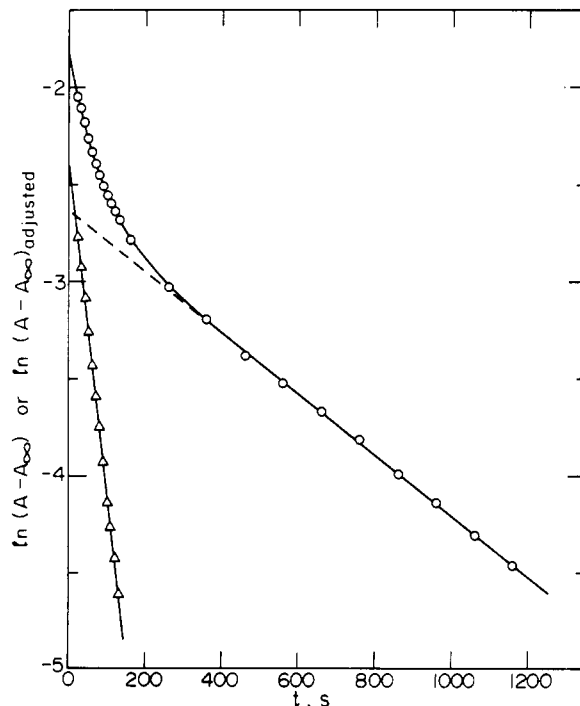

Figure 4. Reaction of methylenecyclooctene with 0.72 M aqueous perchloric acid at 25 °C. The data were analyzed as described in the text: (O) ln $(A - A_\infty)$; (△) lln $(A - A_\infty)_{\text{adjusted}}$.

The first exponential of this expression represents the faster initial drop in A observed in these biphasic reactions. This term will become zero at long times, and a plot of ln $(A - A_\infty)$ measured toward the end of the reaction vs. time should be a straight line. Figure 4 shows that this is so. Extrapolation of this line to shorter times then gives values of the second exponential which can be subtracted from $(A - A_\infty)$, and a plot of the logarithm of this difference vs. time should give another straight line. Figure 4 shows that this is also so.

Individual values of k_1 and k_3 plus the sum $(k_2 + k_{-2})$ may be obtained from the slope and intercept parameters of these two straight lines in combination with measured values of A_∞. This was done for a series of kinetic runs carried out over the range $[\text{HClO}_4]$ = 0.7–1.9 M. The results are summarized in Table S5.[8]

The X_0 function was again used to correlate these data, and good linear relationships were obtained. That for the sum of k_2 and k_{-2}, log $[(k_2 + k_{-2})/C_{\text{H}^+}]$ = –3.066 ± 0.011 + (1.88 ± 0.03)X_0 agrees well with the correlation obtained from the experiments described above in which *cis*-olefin and alcohol were equilibrated directly, log (k/C_{H^+}) = –3.016 ± 0.008 + (1.80 ± 0.02)X_0; this gives strong support to the model (eq 1) upon which this analysis is based. The other two correlations provided by the present data, log (k_1/C_{H^+}) = –2.211 ± 0.029 + (1.82 ± 0.10)X_0 and log (k_3/C_{H^+}) = –2.567 ± 0.037 + (2.22 ± 0.12)X_0, give the dilute solution hydronium ion catalytic coefficients $(k_{\text{H}^+})_1$ = (6.16 ± 0.42) × 10^{-3} M^{-1} s^{-1} and $(k_{\text{H}^+})_3$ = (2.71 ± 0.23) × 10^{-3} M^{-1} s^{-1}. The ratio of these two rate constants, k_3/k_1 = 0.44 ± 0.05, is the (nonequilibrium) proportion of alcohol to *cis*-olefin products formed directly from the *exo*-olefin.

The rate constants determined in this study are summarized in Table II.

Discussion

The results obtained in the present investigation show that the acid-catalyzed interconversion of 1-methyl-*cis*-cyclooctene and its hydration product, 1-methylcyclooctanol, is a simple process which follows a single expo-

Table II. Summary of Rate Constants for Reactions of Olefins and Alcohols in the 1-Methylcyclooctyl System with Aqueous Perchloric Acid at 25 °C
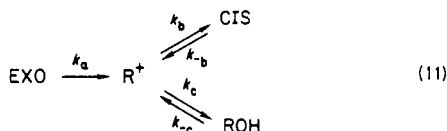
reactn[a]	$10^3 k_{H^+}$, M^{-1} s^{-1}
CIS → ROH	0.538 ± 0.014
ROH → CIS	0.425 ± 0.013
TRANS → CIS + ROH	9930 ± 40
EXO → CIS	6.16 ± 0.42
EXO → ROH	2.71 ± 0.23

[a] CIS = 1-methyl-*cis*-cyclooctene. TRANS = 1-methyl-*trans*-cyclooctene. EXO = methylenecyclooctane. ROH = 1-methylcyclooctanol.

nential rate law and produces slightly more alcohol than olefin at equilibrium, K = [ROH]/[CIS] = 1.27. On the other hand, the acid-catalyzed reactions of the other two olefins of this system, 1-methyl-*trans*-cyclooctene and methylenecyclooctane, though ultimately producing only *cis*-olefin and alcohol in the same equilibrium proportions ([ROH]/[CIS] = 1.27), are complex biphasic processes which initially give *cis*-olefin and alcohol products in nonequilibrium amounts; these nonequilibrium amounts, moreover, are different from one another: [ROH]/[CIS] = 0.44 for methylenecyclooctane and [ROH]/[CIS] = 15 for 1-methyl-*trans*-cyclooctene. This behavior can be understood in terms of the generally accepted mechanism for the acid-catalyzed hydration of simple olefins in which formation of a carbocationic intermediate through protonation of the carbon–carbon double bond is followed by hydration of this cation to final alcohol product, eq 10.[2]

$$\text{>C=C<} \xrightarrow{\text{HA}} \text{H—C—C<}^+ \xrightarrow{\text{H}_2\text{O}} \text{H—C—C—OH} \quad (10)$$
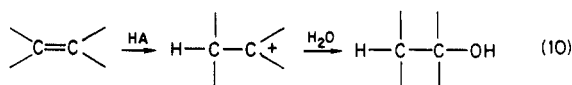
cis- and exo-olefins. Let us first consider the reactions of 1-methyl-*cis*-cyclooctene and methylenecyclooctane with aqueous acid. This can be discussed by using the reaction mechanism shown in eq 11, which is an elaboration of the

$$\text{EXO} \xrightarrow{k_a} \text{R}^+ \underset{k_{-c}}{\overset{k_b, k_{-b}, k_c}{\rightleftharpoons}} \begin{matrix}\text{CIS} \\ \text{ROH}\end{matrix} \quad (11)$$

scheme, eq 1, used before to analyze this system in terms of the phenomenological rate constants k_1, k_2, k_{-2}, and k_3. These phenomenological rate constants are related to those of eq 11 in the following way: $k_1 = k_a k_b/(k_b + k_c)$, $k_2 = k_{-b} k_c/(k_b + k_c)$, $k_{-2} = k_b k_{-c}/(k_b + k_c)$, and $k_3 = k_a k_c/(k_b + k_c)$.

The ratio of products [ROH]/[CIS] formed directly from EXO is determined by the rate constant ratio k_3/k_1, which is equal to k_c/k_b. The ratio of products at equilibrium, on the other hand, depends upon the value of k_2/k_{-2}, which is equal to $(k_c/k_b)(k_{-b}/k_{-c})$. In order for these two ratios to be the same, k_{-b} must be equal to k_{-c}. This can be so only if the free energies of activation for the formation of R$^+$ from CIS and from ROH are the same, and that requires any difference in stability between CIS and ROH to be carried over intact into the two R$^+$-forming transition states. This is an unlikely situation for any two reactions giving a common product, and it is not the case here. The two product ratios are therefore different, and EXO does not give CIS and ROH products in equilibrium proportions. The reaction of EXO with aqueous acid is therefore biphasic.

This argument holds only if EXO reacts with acid more rapidly than CIS undergoes acid-catalyzed equilibration with ROH; otherwise CIS and ROH, no matter in what proportion they first appear, will equilibrate rapidly and
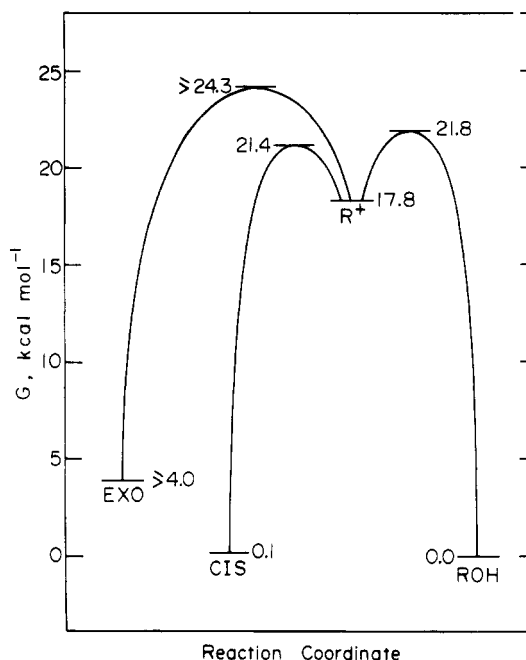

Figure 5. Free energy vs. reaction coordinate diagram for the hydration of methylenecyclooctane (EXO) and 1-methyl-*cis*-cyclooctene (CIS) to 1-methylcyclooctanol (ROH) in 1.00 M acid at 25 °C.

no deviation from a nonequilibrium product distribution will be apparent. This condition is of course fulfilled here: EXO is more reactive than CIS or ROH, but it is interesting that the transition state for the reaction of EXO with acid is nevertheless of higher free energy than those for the interconversion of CIS and ROH; the first step in the reaction scheme of eq 11 is therefore not reversible, as shown. These conclusions follow from the fact that EXO is considerably less stable than CIS and ROH, and its reaction is fast not because the transition state is stable but because the initial state is unstable.

It is useful to quantify these relationships, and it is convenient to do this on a scale which sets the free energy of ROH, the most stable species in this system, at zero. The equilibrium constant [ROH]/[CIS] = 1.27 gives CIS a free energy of 0.14 kcal mol^{-1} on this scale. We do not have an equilibrium constant involving EXO, for we could not detect this substance in an equilibrated olefin–alcohol aqueous solution. This experiment does show, however, that the proportion of EXO at equilibrium can be no greater than about 0.1%, and this gives it a free energy equal to or greater than 4.0 kcal mol^{-1} above that of ROH. The free energy of activation for the reaction of EXO with acid, in the standard state [H$^+$] = 1.00 M, may be calculated from the rate constant for this process, k_a, which is equal to $k_1 + k_3$; this gives $\Delta G^\ddagger_a$ = 20.3 ± 0.2 kcal mol^{-1} and places this transition state at a point equal to or greater than 24.3 kcal mol^{-1} above ROH. The free energies of the other two transition states may likewise be calculated from $\Delta G^\ddagger_{-b}$ = 21.2 ± 0.3 kcal mol^{-1} and $\Delta G^\ddagger_{-c}$ = 21.8 ± 0.2 kcal mol^{-1}, based upon the relationships $k_{-b} = k_2(1 + k_b/k_c)$ and $k_{-c} = k_{-2}/(1 + k_c/k_b)$, plus the fact that $k_b/k_c = k_1/k_3$. The results, displayed in Figure 5, show that the transition state for reaction of EXO with acid is at least 2.5 kcal mol^{-1} above the higher of the two transition states involved in the interconversion of CIS and ROH. This free energy difference corresponds to a rate factor of at least 70, which is enough to make the reaction of EXO with acid effectively nonreversible.

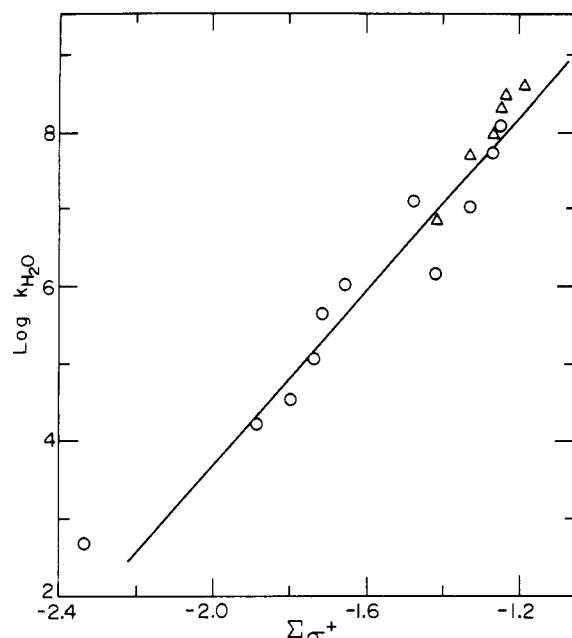The experiments performed here give no information about the free energy level of the cationic intermediate R$^+$.

Figure 6. Correlation of rates of reaction of alkoxy cations with water: ($\triangle$) data from ref 13; (O) data from ref 14.

It is possible, however, to estimate that from pK_R values for a series of structurally similar, i.e., tertiary aliphatic carbocations obtained via a recently published correlation of pK_R's with heats of formation of these ions in superacid media.[12] Data are available for six appropriate systems, and these give an average pK_R which corresponds to ΔG° = 18.3 ± 0.6 kcal mol^{-1} for the process ROH → R$^+$ in 1.00 M acid. Combination of this result with the free energy of activation for the formation of R$^+$ from ROH, given above as $\Delta G^\ddagger_{-c}$ = 21.8 ± 0.2 kcal mol^{-1}, then provides $\Delta G^\ddagger$ = 3.5 ± 0.6 kcal mol^{-1} as the free energy of activation for the reverse process, reaction of R$^+$ with water to give ROH.

It is instructive to compare this free energy of activation for the conversion of R$^+$ to ROH in a tertiary aliphatic system with a value based upon known specific rates of combination of alkoxy-substituted carbocations with water, k_{H_2O}. Such rates have been determined in two different ways, by diffusion-limited trapping of the ions in dilute solution[13] and by direct kinetic measurement in concentrated acid (where the reactions are slow) followed by extrapolation to dilute solution along the correct acidity function;[14] agreement between the two methods is good. We have found that the specific rates of these reactions can be correlated with the sum of σ constants for the three groups directly attached to the cationic center provided that appropriate values of σ^+ [15] are used. This correlation, $\log k_{H_2O}$ = 14.64 ± 0.57 + (5.33 ± 0.37)$\sum \sigma^+$, is illustrated in Figure 6.[16] From it, values of k_{H_2O} for other cations may be estimated. Application to *tert*-butyl gives a rate constant which corresponds to $\Delta G^\ddagger$ = 4.3 ± 0.3 kcal mol^{-1}, in good agreement with the result, $\Delta G^\ddagger$ = 3.5 ± 0.6 kcal mol^{-1},

obtained as described above from the estimated pK_R value for a tertiary aliphatic carbocation. The weighted average of these two values is $\Delta G^\ddagger$ = 4.1 ± 0.3 kcal mol^{-1}, which places R$^+$ on the free energy scale of Figure 5 at 17.8 ± 0.3 kcal mol^{-1} above ROH.

These values of the free energy of activation for reaction of a tertiary aliphatic carbocation with water are remarkably small; they correspond to rate constants of the order of 10^{10} s^{-1}. This is of interest with regard to speculation that such reactions may be essentially unactivated processes[17] and that ions of this kind may be too unstable to exist in nucleophilic solvents.[12,23,18]

The presently studied system is unusual in that comparable amounts of *cis*-olefin and alcohol exist at equilibrium, [ROH]/[CIS] = 1.27. The position of equilibrium for simple olefins in aqueous solution at low temperatures generally lies well to the side of alcohol;[19] for example, for isobutene/*tert*-butyl alcohol, [alcohol]/[olefin] = 7,500 at 25 °C in dilute aqueous solution.[20] The present system is also unusual in that the first transition state on the way from *cis*-olefin to alcohol, that for protonation of the carbon–carbon double bond, is lower than the transition state for hydration of the intermediate cation (see Figure 5); as a consequence the cation goes on to alcohol more slowly than it reverts to olefin: in the terminology of eq 11, k_c/k_b = 0.44. The opposite is again generally the case for simple olefins; for example k_c/k_b = 29 for the isobutene–*tert*-butyl alcohol system and k_c/k_b = 9 for the trimethylethylene–*tert*-amyl alcohol system.[21]

***trans*-Olefin.** The reaction of 1-methyl-*trans*-cyclooctene with aqueous acid is similar to that of methylenecyclooctane in that here again a fast process giving a nonequilibrium distribution of *cis*-olefin and alcohol is followed by a slower equilibration of these products. There is an important difference between the two systems, however, for the initial nonequilibrium product distribution given by the *trans*-olefin, [ROH]/[CIS] = 15.1 ± 0.9 is definitely not the same as that given by the *exo*-olefin, [ROH]/[CIS] = 0.44 ± 0.05. This requires the carbocation intermediate formed by protonation of the *trans*-olefin to be different from that formed from the *exo*-olefin. If this were no so, i.e., if the two carbocations were the same, then this common intermediate would react to give *cis*-olefin and alcohol products with the same rate constants in the two cases, and different initial product distributions would not be observed.

It is likely that the difference between these two carbocations is simply a conformational one. Recent electron diffraction measurements plus molecular mechanics calculations indicate that 1-methyl-*trans*-cyclooctene exists in a twist or crown conformation.[3] Protonation of this molecule should produce a cation with a similar arrangement of ring atoms. The most stable conformation of the 1-methylcyclooctyl cation, on the other hand, is known to be a boat–chair structure,[22] and since methylenecyclooctane has a boat–chair structure as well,[23] it is likely that protonation of this olefin gives the 1-methylcyclooctyl

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cation in this conformation.

Conformational changes in the cyclooctyl system are rapid.[23] But the reaction of tertiary alkyl carbocations with water is also rapid (vide supra), and it is reasonable to assume that the carbocation of crown conformation formed by protonation of 1-methyl-*trans*-cyclooctene is captured by water before very much of it can isomerize to the more stable boat–chair conformation. The structure of 1-methyl-*trans*-cyclooctene, moreover, suggests that the crown cation produced by its protonation will have no hydrogen in a position appropriate to produce 1-methyl-*cis*-cyclooctene by elimination, and it certainly will not react to regenerate the very unstable *trans*-olefin. On this basis, the reaction scheme of eq 12 may be written in which TRANS is 1-methyl-*trans*-cyclooctene and R'^+ and R^+ are the 1-methylcyclooctyl cation in the crown and boat–chair conformations, respectively.

$$\text{TRANS} \longrightarrow R'^+ \xrightarrow{k_d} R^+ \xrightarrow{k_b} \text{CIS} \qquad (12)$$
$$k'_c \searrow \quad \nearrow k_c$$
$$\text{ROH}$$
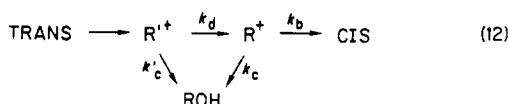
This reaction scheme leads to the expressions given as eq 13 and 14 for the rates of production of ROH and CIS and to eq 15 for the initial product ratio in the reaction of 1-methyl-*trans*-cyclooctene with aqueous acid. Since [ROH]/[CIS] has been determined experimentally (Table I) and k_c/k_b is known from the work on methylenecyclooctane, k'_c/k_d may be evaluated. The result is $k'_c/k_d = 10.2 \pm 1.0$.

$$\frac{d[\text{ROH}]}{dt} = \left(k'_c + \frac{k_c k_d}{k_b + k_c} \right)[R'^+] \qquad (13)$$

$$\frac{d[\text{CIS}]}{dt} = \frac{k_b k_d}{k_b + k_c}[R'^+] \qquad (14)$$

$$\frac{[\text{ROH}]}{[\text{CIS}]} = \frac{k_c}{k_b} + \left(1 + \frac{k_c}{k_b} \right)\frac{k'_c}{k_d} \qquad (15)$$

This rate constant ratio may be used to deduce the height of the barrier for conversion of R'^+ into R^+ in the following way. If the capture of tertiary aliphatic carbocations by water in aqueous solution is an essentially unactivated process, then R'^+ should react with water at half the rate of R^+. This follows from the fact that 1-methyl-*trans*-cyclooctene has one face of its double bond shielded by the methylene groups on the opposite side of the ring, and similar shielding in R'^+ will restrict the attack of water to one face of this cation; R^+, on the other hand, has an open structure with both faces of its cationic center equally available to reaction with water. Thus, with $k_c = 2k'_c$ and $k'_c/k_d = 10.2 \pm 1.0$, $k_c/k_d = 20.4 \pm 2.0$; this makes the barrier for conversion of R'^+ into R^+ 1.8 ± 0.1 kcal mol^{-1} greater than the barrier for reaction of R^+ with water. It was estimated above that the latter is $\Delta G^{\ddagger} = 3.5 \pm 0.6$ kcal mol^{-1}; it follows then that $\Delta G^{\ddagger} = 5.3 \pm 0.6$ kcal mol^{-1} for conversion of R'^+ into R^+, i.e., for isomerization of the crown into the boat–chair conformation of this cation. This result is somewhat less than the barrier, $\Delta G^{\ddagger} = 7.2 \pm 0.1$ kcal mol^{-1} determined for the conformational barrier

which leads to line broadening of the carbon-13 NMR spectrum of the 1-methylcyclooctyl cation.[22] That barrier, however, is for interconversion of two boat–chair conformations. Since the crown conformation of this cation is less stable than the boat–chair conformation, it is likely that the barrier for the crown to boat–chair conformational change in the forward direction would be smaller than that for the interconversion of two boat–chair conformers. It is interesting that the difference between these two barriers, 7.2–5.3 = 1.9 kcal mol^{-1} is of the same order of magnitude as the 2–3 kcal mol^{-1} difference in energy estimated between the crown and chair–boat conformations of cyclooctane itself.[23]

Relative Reactivities. The present results show that both 1-methyl-*cis*-cyclooctene and methylenecyclooctane react with the hydronium ion in dilute aqueous solution at rates which are normal for olefins of this type. The simplest analogue of 1-methyl-*cis*-cyclooctene is the acyclic olefin, 2-methyl-2-butene, for which $k_{H^+} = 2.4 \times 10^{-4}$ M^{-1} s^{-1} has been reported;[24] this is not markedly different from $k_{H^+} = 5.4 \times 10^{-4}$ M^{-1} s^{-1} determined here for 1-methyl-*cis*-cyclooctene, and the latter is also similar to rate constants measured for the cyclic analogues 1-methylcyclohexene, $k_{H^+} = 3.1 \times 10^{-4}$ M^{-1} s^{-1}, and 1-methylcyclopentene, $k_{H^+} = 9.2 \times 10^{-4}$ M^{-1} s^{-1}.[25] The rate constant determined here for methylenecyclooctane, $k_{H^+} = 8.8 \times 10^{-4}$ M^{-1} s^{-1}, is also comparable to that reported for its simplest analogue, isobutene: $k_{H^+} = 3.7 \times 10^{-4}$ M^{-1} s^{-1}.[26]

1-Methyl-*trans*-cyclooctene, on the other hand, is orders of magnitude more reactive, in keeping with its considerable strain energy. The present results put its reactivity toward the aqueous hydronium ion at 18 500 times that of the cis isomer. This is an order of magnitude greater than the strain relief acceleration of reaction with the same reagent shown by the parent unmethylated pair, *trans*- and *cis*-cyclooctene,[27] but an order of magnitude less than the acceleration estimated for the bicyclic *trans*-cyclooctene derivative, bicyclo[3.3.1]non-1-ene.[28]

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